Valorization of carbohydrates: dehydration of sorbitol to isosorbide in the presence of acidic zeolites

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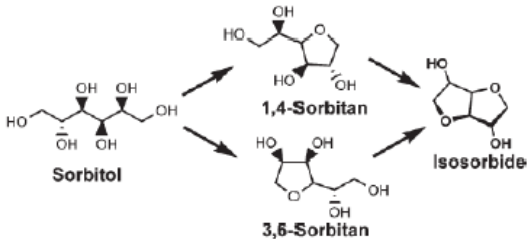
Introduction

Currently, the growing interest in the use of biomass as a renewable and sustainable raw material for the production of energy, chemicals and biofuels is driving the development of new catalytic processes and technologies for its conversion. In this context, the transformation of lignocellulosic biomass can lead to a variety of platform chemicals [1], with a broad spectrum of applications. Sorbitol is one of the useful biomass-derived chemicals that is obtained by catalytic hydrogenation of glucose, which subsequent dehydration and intramolecular cyclization in acid medium [2] gives rise to the formation of isosorbide (Scheme 1). This is a high value-added chemical widely used as intermediate in the pharmaceutical industry, additive polymers such as polyethylene terephthalate (PET) [3] and production of biodegradable polymers.



Scheme 1. Transformation of sorbitol into isosorbide

Mineral acids such as sulphuric and hydrochloric acids have efficient catalytic properties for dehydration of sorbitol [4]. However, the well-known drawbacks associated to homogeneous catalysis have promoted the studies of heterogeneous catalytic processes.

Thus, solid acid catalysts such as zeolites [5], tetravalent metal phosphates [6] and sulfated copper oxide [7] have been reported as alternative solid catalysts. Nevertheless, sometimes, drastic experimental conditions are required to reach a high catalytic activity. In the present work, different commercial zeolites, in their protonic form, have been evaluated as acid solid catalysts for sorbitol dehydration, and several experimental variables have been optimized.

Materials and Methods

The commercial NH_4^+-zeolites have been transformed into the protonated form by calcination. Catalytic dehydration of sorbitol to isosorbide was studied in batch reactors with magnetic stirring in the absence of water, by using molten sorbitol into a silicone bath. Reaction products were identified and quantified by high performance liquid chromatography (HPLC) equipped with a multiwavelength UV-visible and refractive index detectors and a column oven.

Catalysts have been characterized by N_2 adsorption–desorption isotherms at -196ºC, X-ray photoelectron spectroscopy (XPS), X ray diffraction (XRD) and temperature-programmed desorption of ammonia (NH_3-TPD).

Results and Discussion

The textural properties, as determined from the adsorption-desorption isotherms of N_2 at -196°C, have evidenced their microporous nature, inferred from the type I isotherms according to the IUPAC classification [5]. However, the hysteresis loop at high relative pressure in the case of the H- β zeolite, together with the high pore volume, reveal the existence of mesopores (Table 1).

Table 1. Textural and acidic properties of zeolites H-ZSM5, H- β and H-Y.

Catalys	S_{BET} ($m^2 \cdot g^{-1}$)	Vp ($cm^3 \cdot g^{-1}$)	Surface Si/Al	TPD- NH_3 ($\mu mol\ m^{-2}$)
H-ZSM5	374	0,271	28,3	2,38
H-β	441	0,853	11,92	2,76
H-Y	595	0,349	1,36	2,77

Regarding the acidity determined from the NH_3-TPD curves, the three zeolites display high acid site density, which are higher in the case of H- β and H-Y zeolites.

Dehydration of sorbitol was conducted at 190 ºC for 6 h, by using 10 wt.% catalyst in molten sorbitol. Figure 1 compares the catalytic performance of the three zeolites. H-β zeolite attains an isosorbide yield of 55% yield, with full conversion of sorbitol. On the other hand, H-Y and H-ZSM5 zeolites showed lower sorbitol conversion, especially H-Y, and selectivities to monodehydration products.

It is necessary to take into account that after the loss of the first water molecule, the intramolecular cyclization considerably increases the steric hindrance, whereby an increase in the pore dimensions could facilitate the accessibility to the acid sites, thus improving the catalytic performance.

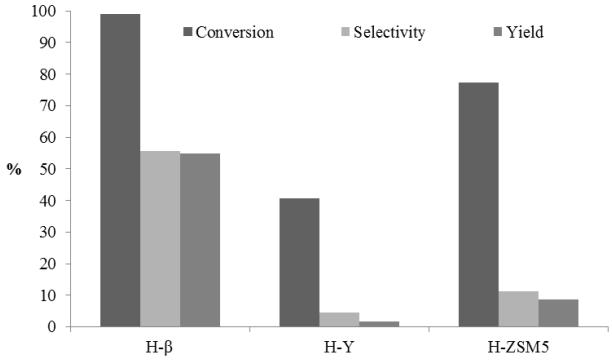


Fig. 1. Sorbitol conversion and isosorbide yield, at 190 ºC after 6 h. (sorbitol/catalyst weight ratio=10)

The reaction was carried out at different reaction temperatures (160-210 ºC) by using H-β zeolite. As can be inferred from Fig. 2, isosorbide yield is notably increased until 175ºC, and a further raising of the reaction temperature doesn't ameliorate the catalytic activity.

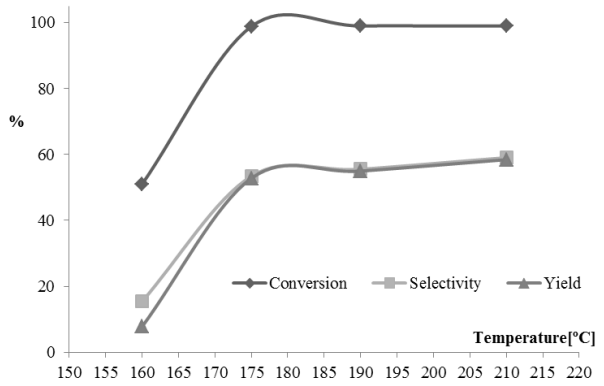


Fig. 2. Influence of the temperature of reaction on the catalytic performance in the presence of H-β, after 90 min at 175ºC. (sorbitol/catalyst weight ratio= 10)

The study of the effect of the catalyst dosage on the conversion of sorbitol to isosorbide has been evaluated at 175ºC for 90 min (Fig. 3). In the absence of catalyst, sorbitol conversion is only 30%, but without formation of isosorbide. However, the sorbitol conversion and isosorbide selectivity are 100% and 55%, respectively, with only 0.1 g of the H-β zeolite. Higher loadings of catalyst doesn't lead to better catalytic performance, perhaps due to diffusional problems, since the stirring rate was maintained constant in this study.

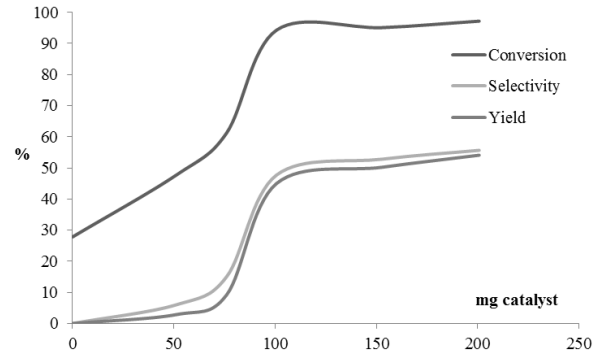


Fig. 3. Effect of the catalyst dosage on the sorbitol dehydration, after 90 min at 175 ºC, by using H-β.

The kinetic of this catalytic process was studied at 175ºC (Fig. 4). Total sorbitol conversion was achieved after 6 h of reaction, though 8 h are required to attain the highest isosorbide yield. These results are in agreement with previous reports [6-8] which suggested the conversion of sorbitol into isosorbide via sorbitan (Scheme 1).

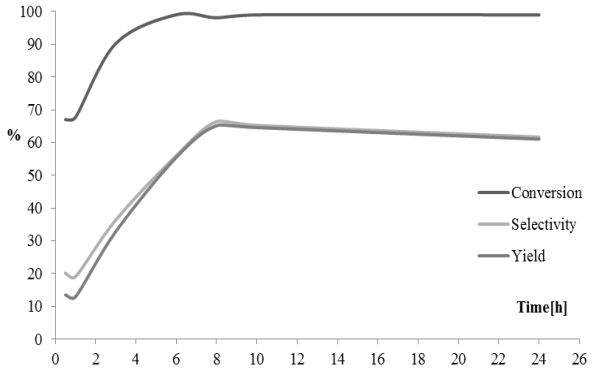


Fig. 4. Kinetic study of sorbitol dehydration, at 175 ºC, in the presence of the H-β zeolite. (sorbitol/catalyst weight ratio=10)

In conclusion, the suitable catalytic performance of the H-β zeolite can be explained not only by its high acidity, but also by the existence of mesopores which favour the access of reactants to the acid sites and the elimination of reaction products. The H-β zeolite can be reused for several catalytic cycles.

Acknowledgements

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